SUPPORTING INFORMATION

On the existence of -agostic bonds: bond analyses of titanium alkyl complexes

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Table S-1. Selected parameters for **1a-5a** calculated at the MP2/6-311++G(3df,2p). Type of arrangement and main geometric and electronic parameters (bond distance (Å), electron density at the BCP, (r e a_0^{-3}), and its Laplacian ^{2} (r e a_0^{-5})) for C-M, C-H, and, when available, QTAIM data for H-H and ring critical point (RCP).

Figure S-2. Graphical representation of overall minima for all studied compounds, calculated at B3LYP/6-311++G(3df,2p) level.

Figure S-3. Example of conformational notation used in this work: Newman's projections for possible conformations of **1b**, **1c**, **2b**, **3b**, **3c**, **4b**, **4c** and **5b** with both H and F substituents, in *eclipsed* and *anti* conformations.

Figure S-4. PES resulting from the variation of the angle for the different possible conformations of **3** and **5**.

Table S-5. Selected BCP parameters for **1-5** calculated at the B3LYP/6-311++G(3df,2p) level. Electron density, (r e a_0^{-3}), its Laplacian, ^{2} (r e a_0^{-5}), ellipticity, and electron energy density, E_d(r) (*hartree*·a_0^{-3}).

Table S-6. QTAIM charges integrated over the atomic basins for the minima and frozen geometries at the indicated $_1$ angles for compounds **1a-5a**, **1d**, **2c**, **3d**, **4d** and **5c**.

Figure S-7. Plots of the Laplacian of the electron density for **1a-5a**, **1d**, **2c**, **3d**, **4d**, and **5c**, including the bond paths, depicted with bold lines. Solid lines indicate charge concentration zones, while dashed lines indicate charge depletion zones.

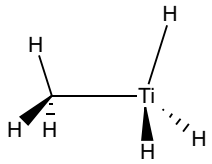
Figure S-8. ELF isosurfaces of compounds **1d**, **2c**, **3d**, **4d**, and **5c** measured at 0.7. Numbering indicates the population of each basin. Same color convention as in Figure 5.

Table S-1. Selected parameters for **1a-5a** calculated at the MP2/6-311++G(3df,2p). Type of arrangement, and main geometric and electronic parameters: Bond distance (Å), electron density (r) ($e \cdot a_0^{-3}$), and its Laplacian ^{2} (r) ($e \cdot a_0^{-5}$) for C-M, C-H, and, when available, QTAIM data for H-H and ring critical point (RCP).

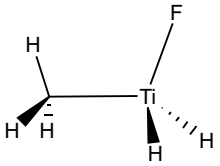
	1a	**2a**	**3a**	**4a**	**5a**
arrangement	-				
$_1$	108.5	91.3	84.2	83.9	164.0
C-M	2.034	1.811	2.055	2.006	1.793
(r)	0.127	0.179	0.118	0.127	0.181
^{2} (r)	0.013	0.158	0.030	0.069	0.156
C-H*agostic*	1.093	1.115	1.149	1.134	1.148
(r)	0.268	0.242	0.239	0.261	0.235
^{2} (r)	-0.908	-0.695	-0.701	-0.879	-0.644
C-H*non-agostic*	1.093	1.084	1.087	1.084	-
(r)	0.268	0.279	0.282	0.291	-
^{2} (r)	-0.908	-1.015	-1.011	-1.129	-
H-H	2.974	2.534	1.796	1.773	2.141
(r)	-	-	0.037	0.037	-
^{2} (r)	-	-	0.061	0.065	-
RCP					
(r)	-	-	0.037	0.036	-
^{2} (r)	-	-	0.067	0.102	-

Figure S-2. Graphical representation of overall minima for all studied compounds, calculated at B3LYP/6-311++G(3df,2p) level.

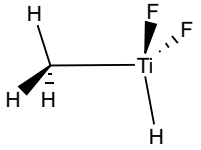
1a$^{e}_{H}$



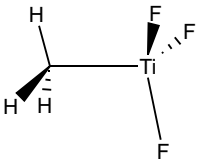
1b$^{e}_{F}$



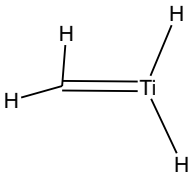
1c$^{a}_{F}$



1d$^{a}_{F}$



2a$^{e}_{H}$



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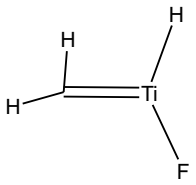
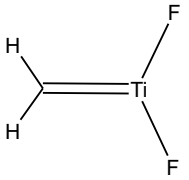
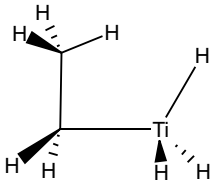


2c$^{e}_{F}$



3a$^{e}_{H}$



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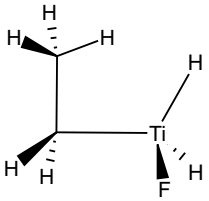
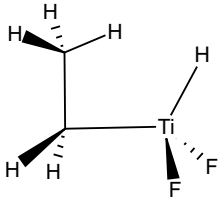
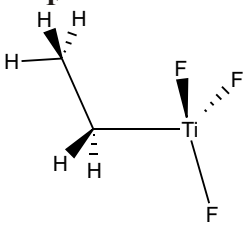


3c$^{e}_{H}$



3d$^{a}_{F}$



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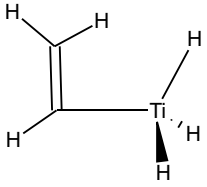
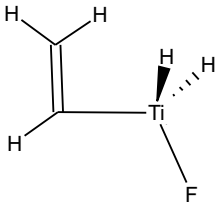
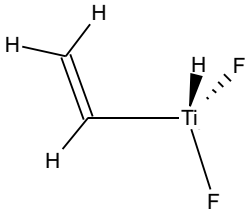


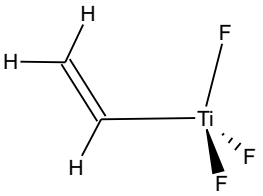
4b$^{a}_{F}$



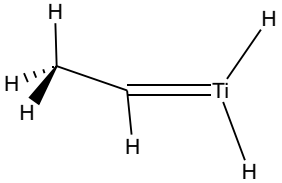
4c$^{a}_{F}$



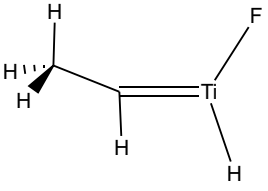
4d$^{e}_{F}$



5a$^{e}_{H}$



5b$^{e}_{F}$



5c$^{e}_{F}$

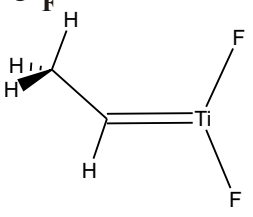


Figure S-3. Example of conformational notation used in this work: Newman's projections for possible conformations of **1b**, **1c**, **2b**, **3b**, **3c**, **4b**, **4c** and **5b** with both H and F substituents, in eclipsed conformations. Referencing substituents (agostically distorted bond and the eclipsed ones) are indicated in bold.

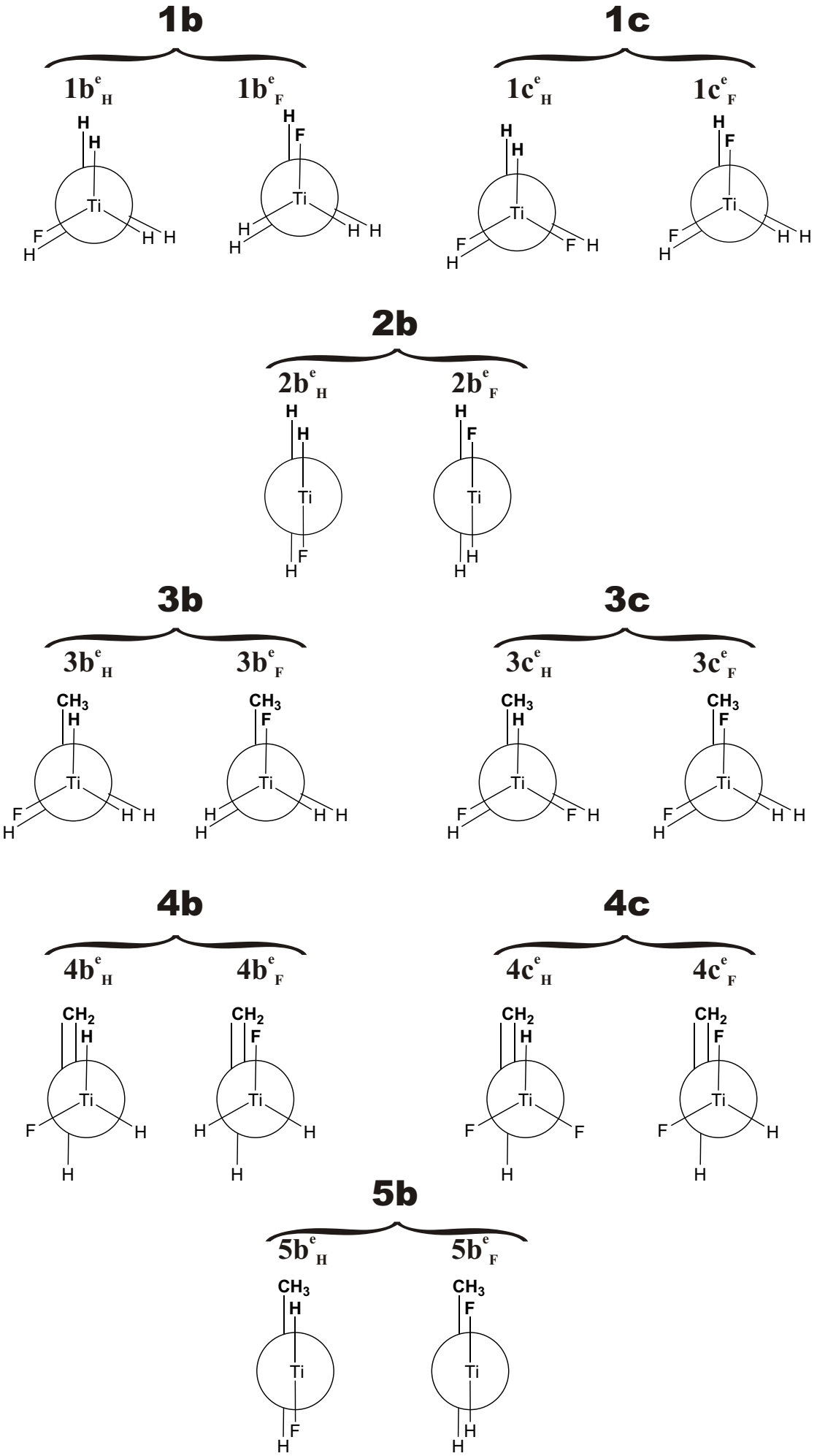


Figure S-3. *(Continued)* Example of conformational notation used in this work: Newman's projections for possible conformations of **1b**, **1c**, **3b**, **3c**, **4b**, and **4c** with both H and F substituents, in *anti* conformations. Referencing substituents (agostically distorted bond and that in *anti* position) are indicated in bold.

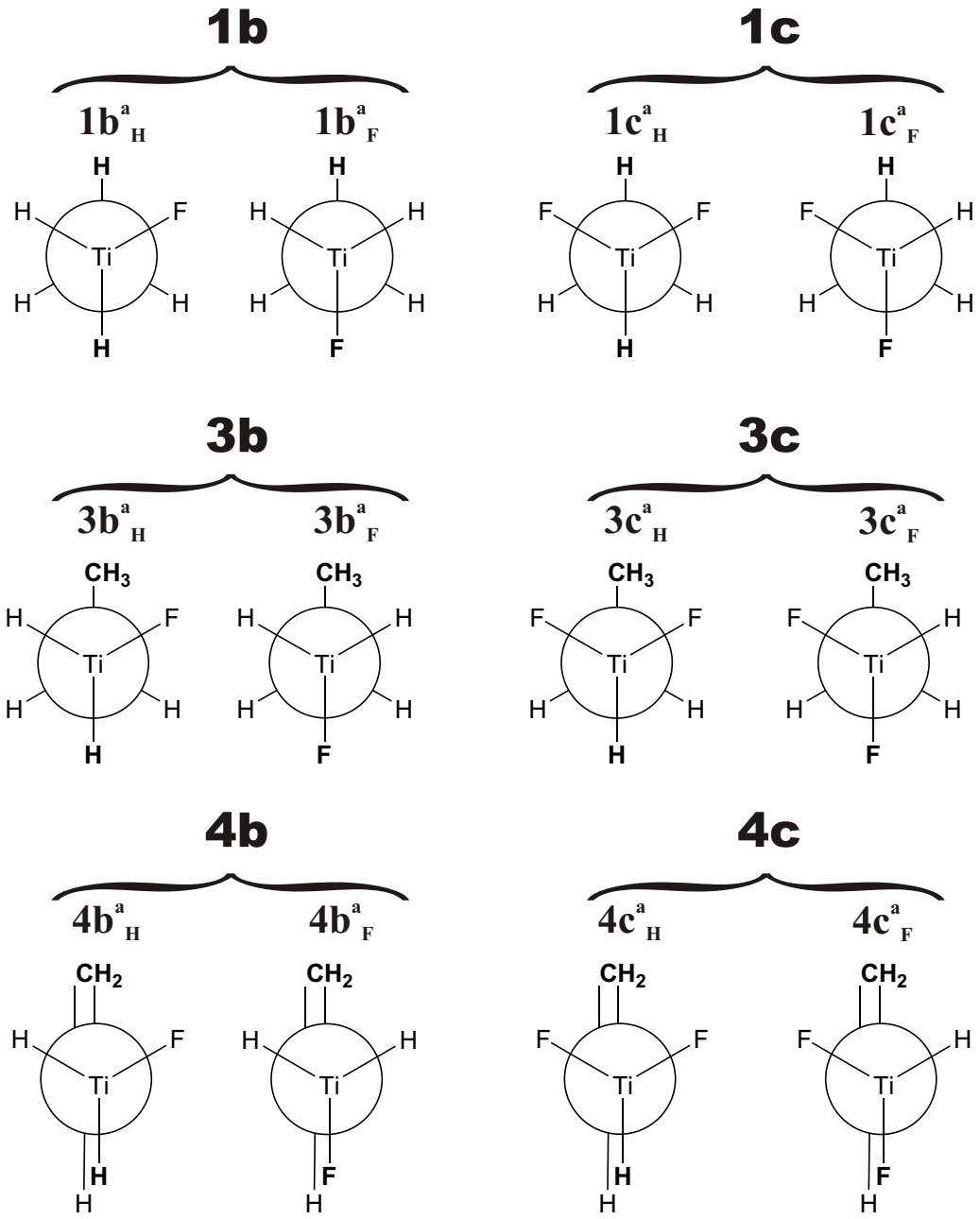
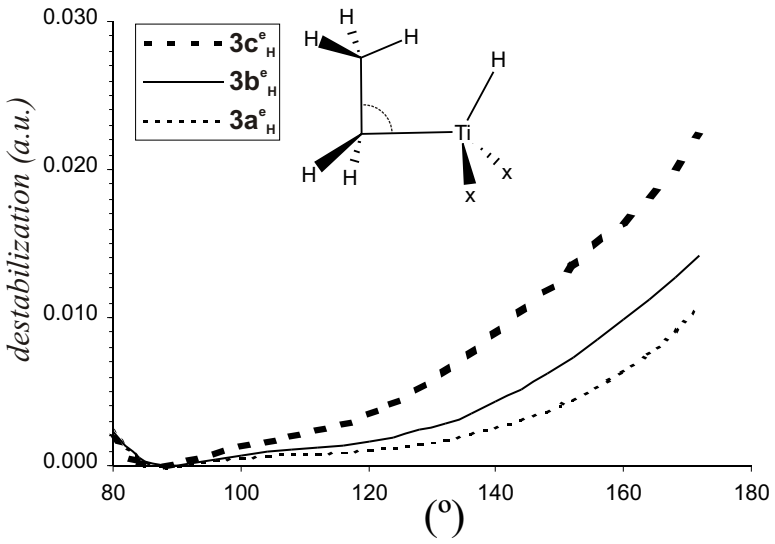
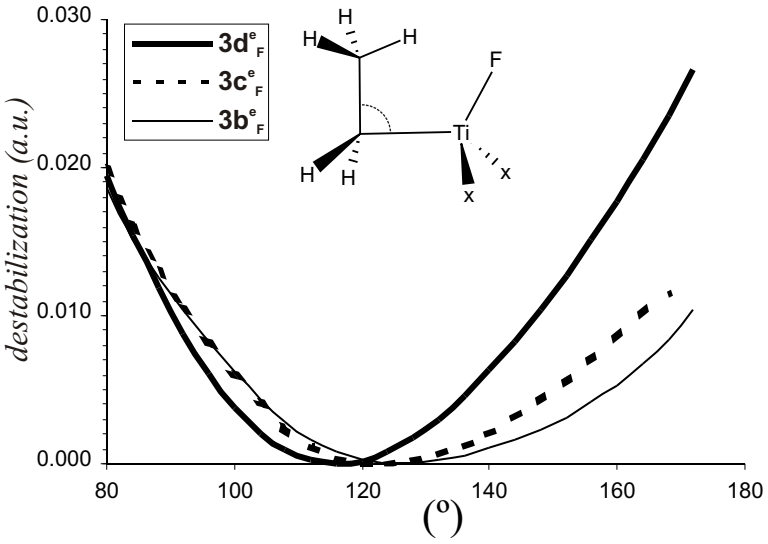
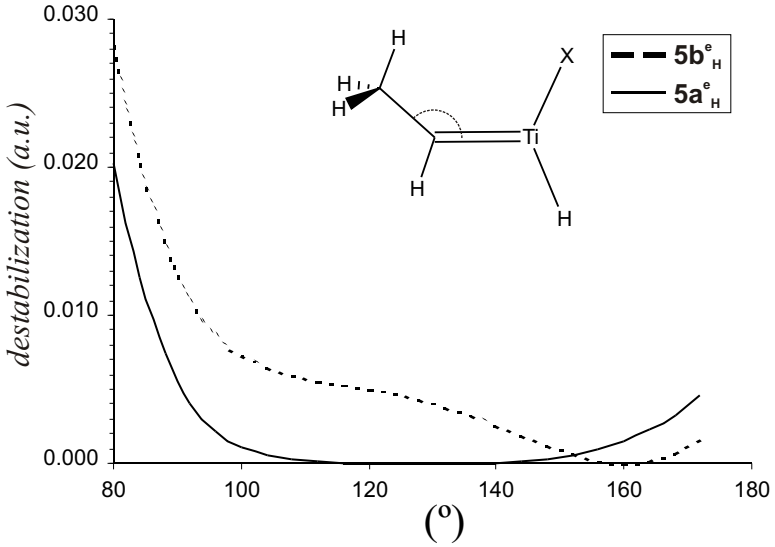


Figure S-4. PES resulting from the variation of the angle for the different possible conformations of **3** and **5**.







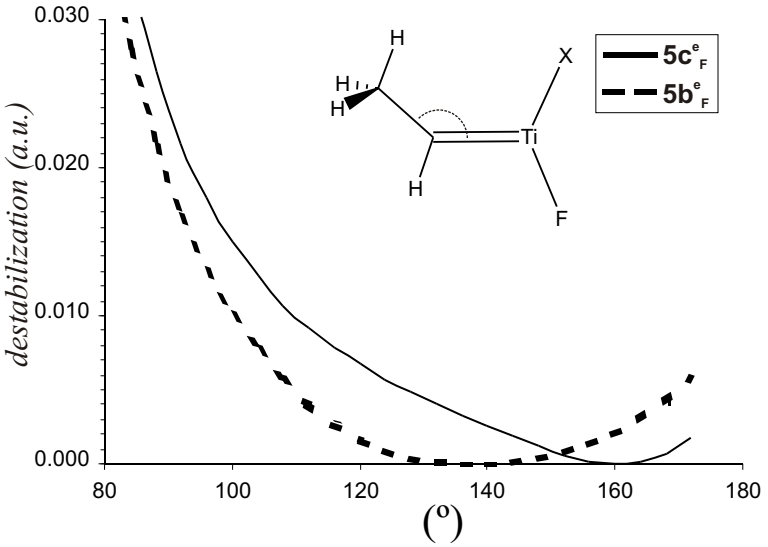


Table S-5. Selected BCP parameters for **1-5** calculated at the B3LYP/6-311++G(3df,2p) level. Electron density, (r) ($e \cdot a_0^{-3}$), its Laplacian, ^{2} (r) ($e \cdot a_0^{-5}$), ellipticity, and electron energy density, E_d(r) (hartree$\cdot a_0^{-3}$).

	bond [a,b]	(r)	^{2} (r)		E_d (r)		*bond* [a,b]	(r)	^{2} (r)		E_d (r)
1a	C -Ti	0.126	0.018	0.00	-0.060	**1d**	C -Ti	0.123	-0.002	0.00	-0.057
	Ti-H_X	0.108	-0.014	0.00	-0.049		Ti-F_X	0.153	0.837	0.03	-0.380
	Ti-H_X	0.108	-0.014	0.00	-0.049		Ti-F_X	0.153	0.837	0.03	-0.380
	C-H	0.269	-0.900	0.05	-0.275		C-H	0.273	-0.930	0.03	-0.281
	C-H	0.269	-0.900	0.05	-0.275		C-H	0.273	-0.930	0.03	-0.281
2a	C -Ti	0.173	0.238	0.68	-0.101	**2c**	C -Ti	0.167	0.199	0.84	-0.095
	Ti-H_X	0.097	0.036	0.08	-0.039		Ti-F_X	0.137	0.797	0.01	-0.026
	Ti-H_X	0.095	0.046	0.02	-0.037		Ti-F_X	0.137	0.797	0.01	-0.026
	C-H	0.254	-0.788	0.03	-0.250		C-H	0.274	-0.952	0.03	-0.284
	C-H	0.280	-1.008	0.00	-0.295		C-H	0.274	-0.952	0.03	-0.284
3a	C -Ti	0.120	0.027	0.04	-0.055	**3d**	C -Ti	0.124	-0.009	0.02	-0.059
	C -C	0.243	-0.513	0.13	-0.198		C -C	0.237	-0.504	0.05	-0.186
	Ti-H_X	0.104	0.012	0.12	-0.045		Ti-F_X	0.150	0.830	0.03	-0.036
	Ti-H_X	0.107	-0.013	0.01	-0.048		Ti-F_X	0.150	0.831	0.04	-0.036
	C -H	0.250	-0.765	0.00	-0.239		C -H	0.279	-0.971	0.01	-0.288
	C -H	0.282	-0.997	0.01	-0.294		C -H	0.273	-0.926	0.05	-0.281
	H - H_X	0.0286	0.046	1.45	-0.003		H -F_X	-	-	-	-
	RCP	0.0278	0.099	-	-		RCP	-	-	-	-
4a	C -Ti	0.119	0.083	0.01	-0.053	**4d**	C -Ti	0.126	0.021	0.08	-0.059
	C -C	0.354	-1.071	0.15	-0.427		C -C	0.347	-1.057	0.24	-0.408
	Ti-H_X	0.104	0.011	0.08	-0.045		Ti-F_X	0.152	0.833	0.02	-0.037
	Ti-H_X	0.108	-0.017	0.01	-0.049		Ti-F_X	0.153	0.837	0.02	-0.038
	C -H	0.261	-0.848	0.02	-0.256		C -H	0.290	-1.069	0.00	-0.306
	C -H	0.284	-1.032	0.01	-0.298		C -H	0.280	-0.994	0.02	-0.292
	H - H_X	0.0298	0.057	3.09	-0.002		H -F_X	-	-	-	-
	RCP	0.0297	0.079	-	-		RCP	-	-	-	-
5a	C -Ti	0.304	0.277	0.74	-0.095	**5c**	C -Ti	0.163	0.216	0.95	-0.090
	C -C	0.257	-0.613	0.01	-0.221		C -C	0.251	-0.580	0.00	-0.211
	Ti-H_X	0.091	0.056	0.03	-0.034		Ti-F_X	0.135	0.789	0.03	-0.025
	Ti-H_X	0.095	0.042	0.09	-0.037		Ti-F_X	0.134	0.778	0.01	-0.024
	C -H	0.281	-0.991	0.01	-0.292		C -H	0.282	-0.997	0.02	-0.294
	C -H	0.276	-0.958	0.01	-0.285		C -H	0.276	-0.954	0.01	-0.284
	C -H	0.249	-0.744	0.01	-0.240		C -H	0.270	-0.910	0.03	-0.275

[a] , and X designate those hydrogen atoms connected to C , C and Ti, respectively.

[b] || and symbols indicate which atom H (or F) lies on the symmetry plane and not, respectively; except in the case of compounds with double bonds, (**2** and **5**) where || identifies the atom closest to the area where agostic approach takes place.

Table S-6. QTAIM charges integrated over the atomic basins for minima and frozen geometries at the indicated $_1$ angle values for compounds **1a-5a**, **1d**, **2c**, **3d**, **4d** and **5c**.

	$_1$ [a]	H$_{\|\|}$ [b]	H	C	H$_{\|\|}$	H	C	Ti	X$_{\|\|}$	X
1a	(88)	-	-	-	-0.02	0.02	-0.41	1.84	-0.48	-0.48
	109.0	-	-	-	0.01	0.01	-0.42	1.85	-0.48	-0.48
1d	(88)	-	-	-	0.00	0.03	-0.38	2.25	-0.65	-0.64
	108.9	-	-	-	0.01	0.01	-0.37	2.25	-0.64	-0.64
2a	91.3	-	-	-	-0.01	0.04	-0.67	1.76	-0.54	-0.57
	(120)	-	-	-	0.02	0.02	-0.68	1.75	-0.56	-0.56
2c	(88)	-	-	-	-0.03	0.06	-0.69	2.01	-0.68	-0.67
	123.3	-	-	-	0.02	0.02	-0.65	1.98	-0.69	-0.69
3a	88.7	-0.04	0.01	0.00	-	0.01	-0.35	1.82	-0.49	-0.49
	(104)	-0.03	0.00	0.05	-	0.00	-0.37	1.83	-0.50	-0.48
3d	(88)	0.02	0.00	0.00	-	0.01	-0.32	2.23	-0.67	-0.63
	113.5	-0.01	-0.01	0.06	-	-0.01	-0.32	2.26	-0.65	-0.65
4a	87.7	0.00	0.06	-0.16	0.06	-	-0.34	1.83	-0.49	-0.48
	(120)	0.01	0.02	-0.03	0.02	-	-0.43	1.86	-0.49	-0.48
4d	(88)	0.03	0.05	-0.14	0.07	-	-0.34	2.26	-0.67	-0.63
	121.1	0.03	0.03	-0.01	0.03	-	-0.42	2.26	-0.64	-0.64
5a	(88)	-0.01	-0.01	0.09	-0.04	-	-0.62	1.72	-0.59	-0.55
	(120)	-0.01	-0.01	0.09	-0.04	-	-0.62	1.72	-0.59	-0.54
	160.6	-0.01	-0.01	0.09	-0.04	-	-0.62	1.72	-0.55	-0.59
5d	(88)	0.00	0.00	-0.02	0.04	-	-0.58	1.97	-0.73	-0.68
	137.3	-0.01	-0.01	0.09	0.00	-	-0.60	1.94	-0.70	-0.70

[a] Values in parenthesis indicate a frozen valence angle, forcing agostic or non-agostic conformations

[b] || and symbols indicate which H (or X) atom lies on the symmetry plane and which not, respectively, except in the case of compounds with double bonds, (**2** and **5**), where || identifies the atom closest to the area where agostic approach takes place.

Figure S-7. Plots of the Laplacian of the electron density for **1a**-**5**a, **1d**, **2c**, **3d**, **4d**, and **5c**, including the bond paths, depicted with bold lines. Solid lines indicate charge concentration zones, while dashed lines indicate charge depletion zones.

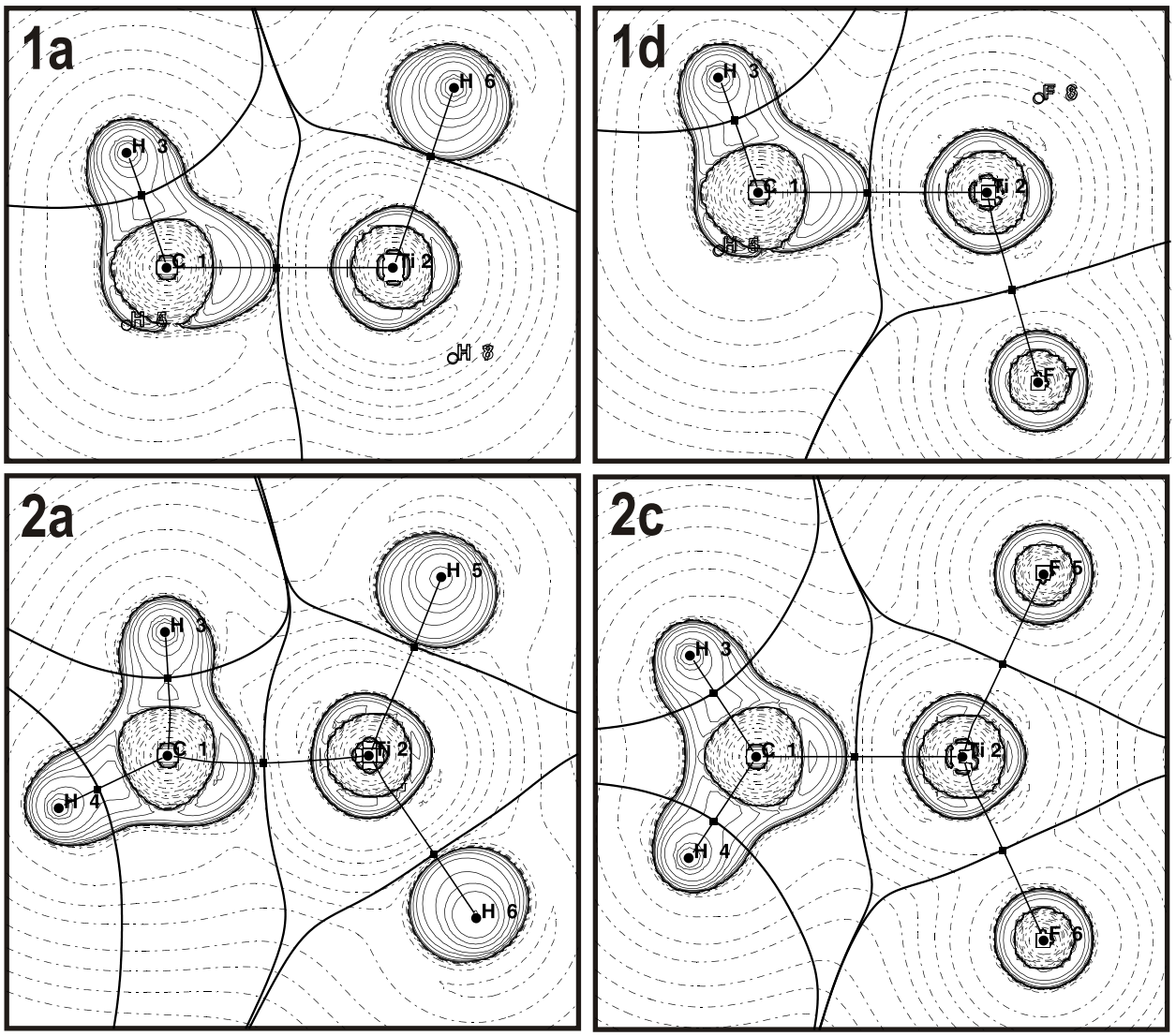


Figure S-7. *(Continued)*

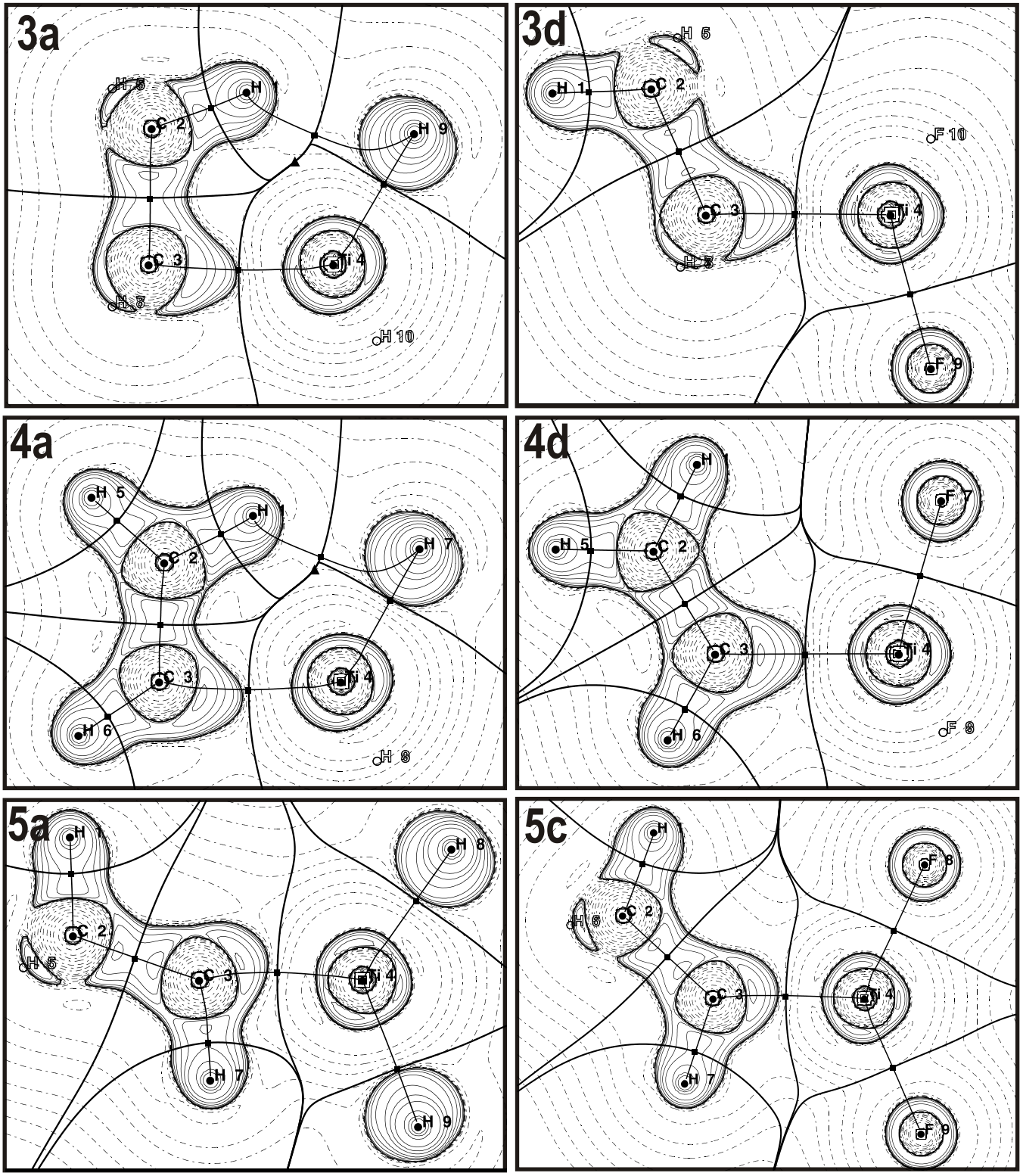


Figure S-8. ELF isosurfaces of compounds **1d**, **2c**, **3d**, **4d**, and **5c** measured at 0.7. Numbering indicates the population of each basin. Same color convention as in Figure 5.